

FABRICATION AND COMPARISON BETWEEN POLYMERIC MEMBRANE  
WITH MIXED MATRIX MEMBRANE ON THEIR PERFORMANCE FOR O<sub>2</sub>/N<sub>2</sub>  
SEPARATION

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A thesis submitted in fulfillment of the requirements for the award of the Degree of  
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**SUPERVISOR'S DECLARATION**

“I hereby declare that I have read this thesis and in my opinion this thesis has fulfilled the qualities and requirements for the award of Bachelor's Degree of Chemical Engineering (Gas Technology).”

Signature: .....

Supervisor's name: Norida Binti Ridzuan

Date: .....

## ABSTRACT

Development of polymeric gas separation membranes is one of the fastest growing branches in membrane technology. There have been many research made on the improvement of the performance of polymeric membranes over the recent years. However, polymeric membranes are somewhat deficient in meeting the requirements of current membrane technology. Therefore, mixed matrix membranes (MMMs), comprising of rigid permeable or impermeable particles such as zeolites, carbon molecular sieves (CMS), silica, and carbon nanotubes, dispersed in a continuous polymeric matrix presents an interesting approach for improving the separation properties of polymeric membranes. The main objective of this study is to compare polymeric membranes with mixed matrix membranes on their performance for O<sub>2</sub>/N<sub>2</sub> separation. This research observed the effect of coating agent, silicone rubber (polydimethylsiloxane) for surface improvement for polymeric membranes and MMMs, as well as the observation of the addition and modification of zeolite 4A using silane coupling agent, 3-aminopropyltrimethoxysilane (APTMOs) in the fabrication of MMMs. The fabrication of asymmetric flat sheet polymeric membranes and MMMs were prepared by using the dry/wet phase inversion technique. The prepared membranes were then coated with silicone rubber diluted in n-hexane in order to decrease the surface defects. Then, the membranes were tested using O<sub>2</sub> and N<sub>2</sub> gases using permeability test rig. The surface and morphology of the samples were identified by using Scanning Electron Microscopy (SEM). From the results obtained, the coating of membrane surface did enhance the selectivity of coated membranes by caulking the defects on the membrane outer surface layer. The incorporation of zeolite into polymer matrix thus somehow improved the performance of plain polymeric membrane by increasing of selectivity with high permeability. Based on the membrane performance results at 4 bar, the highest selectivity was found using coated modified MMMs at the value of 4.42, followed by coated unmodified MMMs at selectivity of 3.35, coated polymeric membranes at selectivity of 1.46, and finally uncoated polymeric membranes at selectivity of 1.44. The modification of zeolite surface using silane coupling agent improved the adhesion between zeolite and polymer which has increased the selectivity tremendously compared to the unmodified zeolite. Therefore, it is strongly agreed that coated modified MMMs is an alternative way to replace polymeric membranes for the application of membrane-based gas separation.

## ABSTRAK

Pembangunan membran polimer untuk pemisahan gas merupakan salah satu cawangan yang pesat berkembang dalam teknologi membran dan banyak penyelidikan telah dibuat ke atas peningkatan prestasi membran polimer sejak kebelakangan ini. Akan tetapi, membran polimer mempunyai kelemahan dalam memenuhi keperluan teknologi membran terkini dan membran campuran matrik (MMM), terdiri daripada partikel tegar telap atau tak telap seperti zeolit, ayak molekul karbon (CMS), silika, dan karbon nanotub, yang disebarkan dalam matriks polimer yang berterusan, membentangkan satu pendekatan yang menarik untuk meningkatkan sifat-sifat pemisahan membran polimer. Objektif utama kajian ini adalah untuk membandingkan prestasi membran polimer dan MMM untuk pemisahan  $O_2/N_2$ . Kajian ini memperlihatkan kesan ejen salutan, silikon getah (polidimetilsilosan), untuk peningkatan permukaan membran polimer dan MMM, serta pemerhatian dari segi penambahan dan modifikasi zeolit 4A dengan menggunakan ejen gandingan silan, 3-aminopropiltrimetoksisilan (APTMOs) dalam fabrikasi MMM. Teknik fasa balikan kering/basah digunakan untuk menghasilkan membran asimetrik kepingan rata untuk membran polimer dan MMM. Membran yang terhasil disalut dengan silikon getah dan n-heksana untuk mengurangkan kecacatan pada permukaan membran. Membran diuji menggunakan  $O_2$  dan  $N_2$  sebagai ujian gas pada mesin penguji kadar penembusan dan imej permukaan dan keratin rentas membran didapati dengan menggunakan Mikroskop Pengimbas Elektron (SEM). Daripada hasil kajian yang diperolehi, ejen salutan silikon getah telah meningkatkan kebolehmempilihan dengan mengurangkan kecacatan pada permukaan membran. Penambahan zeolit ke dalam matriks polimer telah meningkatkan selektiviti di samping kebolehtelapan yang tinggi. Berdasarkan keputusan prestasi membran pada 4 bar, MMM yang bersalut dan dimodifikasi mencatatkan kebolehmempilihan yang tertinggi iaitu pada 4.42, diikuti dengan MMM yang bersalut dan tidak dimodifikasi pada kebolehmempilihan 3.35, membran polimer yang bersalut pada kebolehmempilihan 1.46, dan akhir sekali membran polimer yang tidak bersalut pada kebolehmempilihan 1.44. Modifikasi permukaan zeolit menggunakan ejen gandingan silan telah meningkatkan adhesi antara zeolit dengan polimer, di samping menunjukkan kebolehmempilihan yang pesat sekali berbanding dengan zeolit yang tidak dimodifikasikan. Oleh yang demikian, MMM yang bersalut dan dimodifikasi merupakan alternatif yang terbaik untuk menggantikan membran polimer untuk aplikasi teknologi membran dalam pemisahan gas.

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## LIST OF ABBREVIATIONS

### Abbreviations

|                 |   |                                |
|-----------------|---|--------------------------------|
| PSF             | - | Polysulfone                    |
| PES             | - | Polyethersulfone               |
| PI              | - | Polyimide                      |
| MMM             | - | Mixed matrix membrane          |
| PDMS            | - | Polydimethylsiloxane           |
| O <sub>2</sub>  | - | Oxygen                         |
| N <sub>2</sub>  | - | Nitrogen                       |
| APTMS           | - | 3-aminopropyl-trimethoxysilane |
| SEM             | - | Scanning electron microscopy   |
| LMWA            | - | Low molecular weight additives |
| TAP             | - | 2, 4, 6-triaminopyrimidine     |
| CO <sub>2</sub> | - | Carbon dioxide                 |
| CMS             | - | Carbon molecular sieves        |
| APDEMS          | - | 3-aminopropyl-diethoxysilane   |
| Da              | - | Dalton                         |
| NMP             | - | 1-methyl-2-pyrrolidone         |
| EtOH            | - | Ethanol                        |

**Parameters/Symbols**

|               |   |                          |
|---------------|---|--------------------------|
| P             | - | Permeability             |
| D             | - | Diffusivity coefficient  |
| S             | - | Solubility coefficient   |
| Q             | - | Gas flow rate            |
| A             | - | Membrane area            |
| $\Delta P$    | - | Pressure difference      |
| $P_A$         | - | Permeability of gas A    |
| $P_B$         | - | Permeability of gas B    |
| (P/l)         | - | Pressure-normalized flux |
| GPU           | - | Gas permeation unit      |
| wt%           | - | Weight percentage        |
| $\alpha_{AB}$ | - | Selectivity of membrane  |

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 BACKGROUND OF STUDY**

The studies of membranes can be traced back to the eighteenth century which had been done by a number of philosopher scientists. The systematic studies of membranes were first made in laboratory scale until Loeb and Sourirajan transformed membrane separation from laboratory scale to an industrial process by developing the Loeb-Sourirajan process for making defect-free, high-flux, anisotropic reverse osmosis membranes in the early 1960s (Baker, 2004). As years come and go, the development of membrane separation technology has increased as many studies have been made and improved by previous researchers, thus membranes have gained an important place in separation technology and are now used in wide range of applications. As a general definition, membrane acts as a barrier, which separates two phases and restricts transport of various chemicals in selective manner (Ravanchi *et. al.*, 2009). The applications of membrane range from desalination, dialysis, and filtration to gas separation (Norida, 2004).

Throughout chemical industries, gas separation is an important unit operation. During the last few decades, the membrane-based gas separation technology has held a part of market share in competition with traditional separation process (cryogenic distillation and adsorbent bed processes) due to its various advantages such as low capital investment, ease of operation, low energy consumption, and also environmental friendly (Javaid, 2005; Li *et. al.*, 2006a). Nowadays, gas separation membranes find

many applications such as hydrogen separation, oxygen-hydrogen separation, natural gas separation (carbon dioxide separation, dehydration, and dew point adjustment), vapor-vapor separation, and dehydration of air (Aroon *et. al.*, 2010).

Gas separation in membrane occurs due to differences in permeabilities of the species flowing through the membrane. The performance of membrane-based gas separation depends solely on the permeability and selectivity of the membranes. Membrane with high permeability leads to high productivity and low capital costs, whereas membrane with high selectivity leads to more efficient separations, higher recovery, and lower power costs. Broadly, membranes used for gas separation can be categorized into two major classes: porous inorganic and dense polymeric (Javaid, 2005). The majority of membrane materials for gas separation are polymeric; however, there is a steady growth in the application of inorganic materials such as ceramic, metal, carbon, and glass membranes (Norida, 2004). Polymeric materials such as polysulfone (PSF), polyethersulfone (PES), and polyimide (PI) exhibit high selectivity coefficients and acceptable permeability values for separation of gas mixture (Ismail *et. al.*, 2008a). Polymeric membranes are the most popular membranes because of their high performance, easy synthesis, long life, good thermal stability, adequate mechanical strength, and high resistance to gases and chemicals (Sadrzadeh *et. al.*, 2009).

Polymeric membranes have their own downsides that limit their industrial applications. The performance of polymeric membranes would deteriorate when they are used in harsh environment (Vu, 2001; Ismail *et. al.*, 2008a). Robeson (1991) showed that in selectivity versus permeability plot, the data for many polymeric membranes with respect to a specific gas pair lie on or below a straight line defined as the upper bound tradeoff curve (Robeson, 1991; Li *et. al.*, 2006a; Ismail *et. al.*, 2008a; Aroon *et. al.*, 2010). This phenomena has led to the growing interest in the development of gas separation membrane based on materials that provide better selectivity, thermal stability, and chemical stability than those already existed (Saufi & Ismail, 2002; Ismail *et. al.*, 2008a).



To expand the industrial application of membrane separation technology, mixed matrix membranes have been proposed as an alternative approach to obtain high selectivity benefits. Mixed matrix membranes are obtained by embedding numerous types of fillers such as carbon molecular sieves, mesoporous molecular sieves, activated carbon, silica or conductive polymers, but mostly zeolites into a polymer matrix (Sen *et. al.*, 2007; Karatay *et. al.*, 2010; Vu *et. al.*, 2003). Inorganic molecular sieves like zeolites and carbon molecular sieves are excellent materials with diffusivity selectivity significantly higher than polymeric materials. Membranes used for gas separation comprises various zeolites with large-pore ( $Y$ -type,  $X$ ,  $\beta$ ), medium-pore (ZSM-5, FER), and small-pore ( $A$ -type, SAPO-34) (Chung *et. al.*, 2007).

The investigation of mixed matrix membranes for gas separation was first reported in 1970s with the discovery of a delayed diffusion time lag for  $\text{CO}_2$  and  $\text{CH}_4$  when adding zeolite 5A into rubbery polymer polydimethylsiloxane (PDMS) from Paul and Kemp's work. They found that the addition of zeolite 5A into the polymer matrix caused very large increases in the diffusion time lag but had only minor effects on the steady-state permeation (Chung *et. al.*, 2007; Li *et. al.*, 2006a; Aroon *et. al.*, 2010).

## 1.2 PROBLEM STATEMENT

As been stated earlier, the permeability and selectivity values of membranes should be as high as possible for industrial gas separation applications to work efficiently and effectively. According to Ahn and coworkers (2008), mixed matrix membrane is considerably influenced by several factors, i.e. (a) polymer and inorganic material properties, (b) their compatibility and absence of interfacial defects, (c) morphology, and (d) membrane formation process. Meanwhile for polymeric membranes, the morphology and separation performance are influenced by factors such as different types of non-solvent additive (NSA), rheological effect, polymer concentration, and evaporation condition during membrane fabrication (Norida, 2004). Although both factors affecting polymeric membrane and mixed matrix membrane are

almost similar, the performance of gas separation for both types of membranes differs greatly. Therefore, this research study aims to compare polymeric membrane with mixed matrix membrane on their performance for gas separation.

### **1.3 RESEARCH OBJECTIVES**

Based on the problem statement described above, the following objectives can be done as follows:

- a) To compare the performance of developed mixed matrix membrane with polymeric membrane using oxygen and nitrogen as test gases.
- b) To compare the performance of developed mixed matrix membrane prepared from unmodified and modified zeolite 4A using oxygen and nitrogen as test gases.
- c) To identify which type of membrane exhibits the best performance for O<sub>2</sub>/N<sub>2</sub> separation.

### **1.4 SCOPES OF RESEARCH**

In order to achieve the following objectives described above, the following scopes are drawn:

- a) Fabrication of asymmetric flat sheet polymeric membrane and mixed matrix membrane using dry/wet phase inversion technique.
- b) Modification of zeolite 4A using 3-aminopropyl-trimethoxysilane (APTMOs) as a coupling agent.
- c) Introduction of coating agent (silicone rubber) for surface improvement.

- d) Performance characterization of polymeric membrane and mixed matrix membrane using N<sub>2</sub> and O<sub>2</sub> as test gases.
- e) Study of morphology on the surface layer and cross-section of polymeric membrane and mixed matrix membrane using Scanning Electron Microscopy (SEM).

## **1.5 RATIONALE AND SIGNIFICANCE**

Membrane technology is an innovative direct method to carry out gas separations and it is less affected by scale factors and fluctuations of the feed composition than the conventional separation techniques. In fact, membrane units are intrinsically modular (easy scale-up) and compact, working continuously without chemical damage of the involved species. They compete successfully with conventional technologies in virtue of a high flexibility to tolerate feed fluctuations in composition and flow rate and as weight and space requirements are important. Thus, this study focuses on the performance of polymeric membrane and mixed matrix membrane. From doing this research study, many industries will benefit from membrane technology such as improved efficiency in production, low production cost, and more energy is saved, because instead of only using either polymeric membrane or mixed matrix membrane, industries can apply both types of membranes into their industrial applications for membrane separation technology.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 MEMBRANE SEPARATION TECHNOLOGY**

Membrane separation processes have become one of the emerging technologies, which underwent a rapid growth during the past few decades. Membrane process encompasses wide range of applications in fluid separation and it is considered as new and emerging in separation technology for industrial applications. Gas separation became a major industrial application of membrane technology for the past 15 years, but the study of gas separation has long begun since that period (Ismail *et. al.*, 2010). For several important separation processes, membrane technology has now reached its initial stage of maturity (Norida, 2004). There are six developed and a number of yet-to-be-developed industrial membrane technologies and applications as shown in Table 2.1 and Table 2.2 respectively.

**Table 2.1:** Membrane process technologies

| <b>Category</b>   | <b>Process</b>   | <b>Status</b>  |
|---|--|--|
| Developed industrial membrane separation technologies       | Microfiltration, Ultrafiltration, Reverse Osmosis, Electrodialysis | Well established unit operations. No major breakthroughs seem imminent.                          |
| Developing industrial membrane separation technologies      | Gas separation, Pervaporation                                      | A number of plants have been installed. Market size and number of applications are expanding.    |
| To-be-developed industrial membrane separation technologies | Carrier Facilitated Transport, Membrane Contactors, Piezodialysis  | Major problems remain to be solved before industrial systems will be installed on a large scale. |

Source: Baker (2004)

**Table 2.2:** Major membrane processes applications

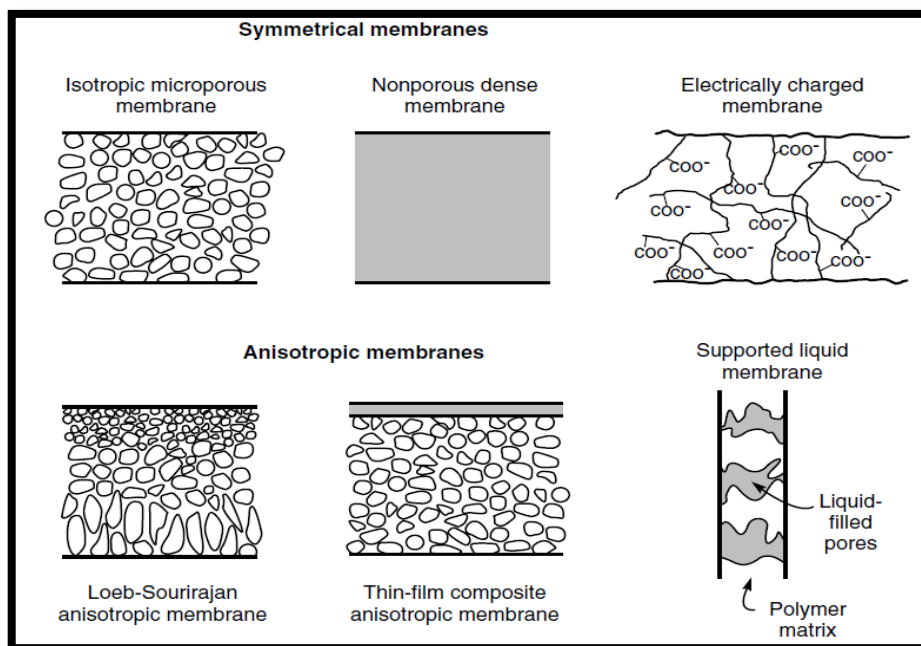
| <b>Membrane Process</b> | <b>Application</b>  |
|-------------------------|---|
| Microfiltration-Cross   | Sterile solution/water purification   |
| Flow Filtration         | Beverage filtration effluents, Cell harvesting  |
| Ultrafiltration         | Dairy (whey recovery, pre-cheese concentration), Electrocoat colloids, Effluents (oil-water, pulp and paper, dye-stuffs, tannery), Biological (enzymes, fermentation), Water purification |
| Reverse Osmosis         | Water desalination, ultrapure water, dairy industry, effluent treatment (metal-finishing, photographic, chemical processes),  |

|                 |   |
|-----------------|---|
|                 | biomedical applications, and pharmaceutical industries  |
| Gas Separation  | Hydrogen recovery/removal, CO <sub>2</sub> removal, O <sub>2</sub> enrichment, helium recovery, N <sub>2</sub> enriched air, pollution control, sour gas treatment, H <sub>2</sub> recovery, natural gas dehydration, air dehydration |
| Electrodialysis | Water desalination, acidity reduction in citrus juice, deionization of whey   |
| Dialysis        | Hemodialysis (artificial kidney)  |
| Pervaporation   | Dehydration of organic solvents   |

Source: Norida (2004)

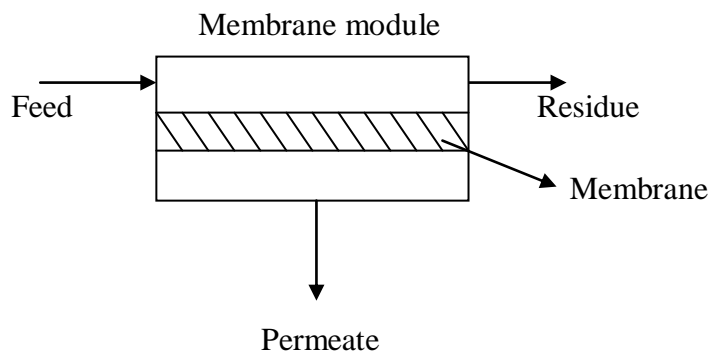
## 2.2 HISTORY OF MEMBRANE TECHNOLOGY

A membrane can be simply defined as an interphase between two bulk phases, where it acts as a barrier which separating two phases and restricting transport of various chemicals in selective manner. A membrane can be homogeneous or heterogeneous, symmetric or asymmetric in structure, solid or liquid; can carry positive or negative charge or be neutral or bipolar. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as 10 microns to few hundred micrometers (Ravanchi *et. al.*, 2009). The principal types of membranes and schematic diagram of the basic membrane gas separation process as shown in Figure 2.1 and Figure 2.2 respectively.



**Figure 2.1:** Schematic diagrams of principle types of membrane

Source: Baker (2004)



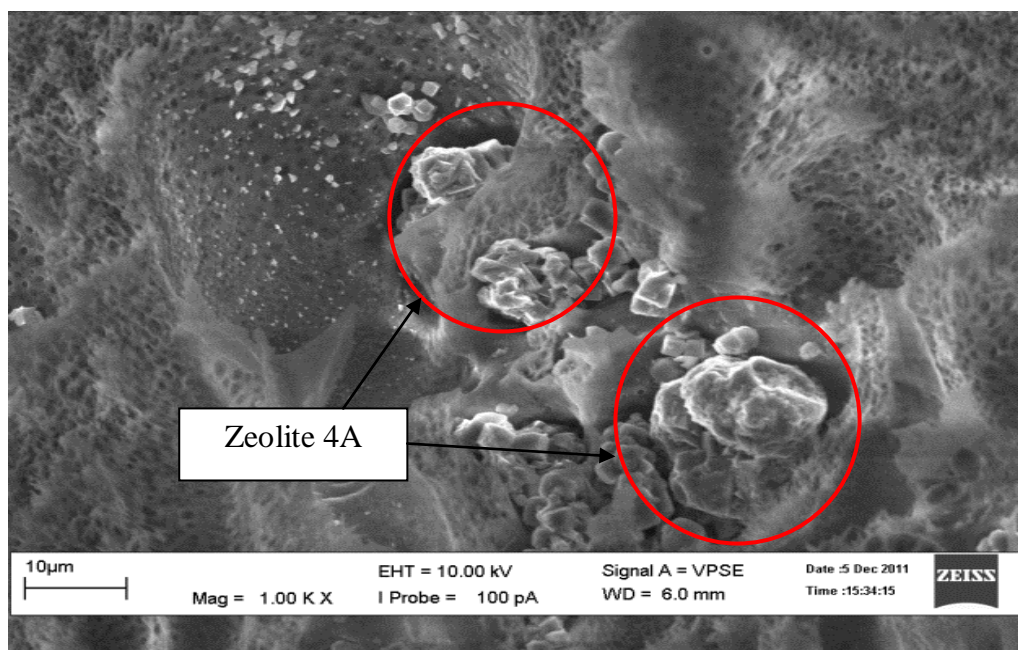
**Figure 2.2:** Schematic diagram of basic membrane for gas separation process

The schematic studies of membrane phenomena can be traced back to the eighteenth century made by a number of philosopher scientists. The historical background of membrane technology is summarized as shown in Table 2.3.

**Table 2.3:** Historical background of membrane technology

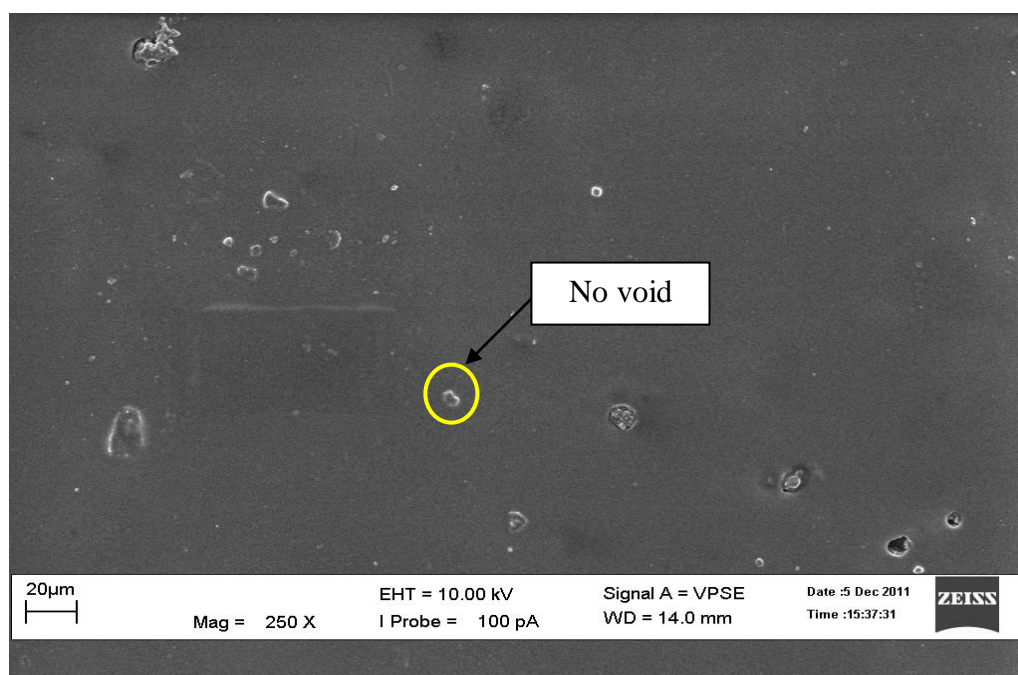
| <b>Name of Inventor</b>   | <b>Year</b> | <b>Invention</b>   |
|---|-------------|--|
| Abbè Nolet  | 1978        | -Coined the word ‘Osmosis’ to describe permeation of water through diaphragm.<br>-Water diffused from dilute to concentrated solution.                             |
| Through the 19 <sup>th</sup> and early 20 <sup>th</sup> centuries, membranes had no industrial or commercial uses, but were used as laboratory tools to develop physical/chemical theories. |             |  |
| Thomas Graham   | 1829        | -Performed the first recorded experiment on the transportation of gases and vapors in polymeric membranes.   |
| Fick  | 1855        | -Proposed the quantitative description of material transport through the boundary layer.   |
|   | 1866        | -Publication of the concepts for gas permeation in term of ‘solution diffusion mechanism’.   |
| The model concept proposed by Fick and Thomas Graham has a significant contribution to the understanding of gas diffusion phenomena across membranes.                                       |             |  |
| Van’t Hoff  | 1877        | -Developed the limit law, which explained the behavior of ideal dilute solutions; directly led to the Van’t Hoff equation.   |
| Maxwell et. al.   |             | -The concept of a perfectly selective semi-permeable membrane was used in developing the kinetic theory of gases.  |
| Bechhold  | 1907        | -The first person to define the relationship between physical properties like the bubble point, surface tension, pore radius, and the performance of the membrane. |
|   |             | -Devised a technique to prepare nitrocellulose membranes for graded pore size, which he determined by bubble test.   |





(b)

**Figure 4.7:** Cross-section area of coated modified MMM at magnification of; (a) 500X, (b) 1000X



**Figure 4.8:** Surface area of coated modified MMM